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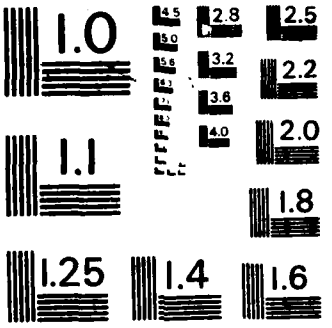

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An Analysis of the Inversion of Ammonia with the Use of Intramolecular Pair Potentials

by

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Abstract

We employ a symmetry-adaptable Taylor series in the evaluation of matrix elements which arise in a variational treatment of the inversion doubling in ammonia. With the use of realistic pairwise N-H potential energy functions, we obtain reasonable agreement with experiment. The analysis could be improved, we suggest, by considering additional degrees of freedom.

A-1

Introduction

The phenomenon of the inversion doubling of the vibrational spectrum of ammonia has been known for more than five decades.[1] During this length of time, the phenomenon has yielded several times to thorough experimental[2] and theoretical[3-8] investigation; it is well-known that the spectral doubling is due ot the tunnelling of the nitrogen atom from one side of the base plane of the three hydrogen atoms to the other. There would seem therefore to be no warrant to pursue yet another investigation merely to improve--by small measure--upon that which already seems to be completely understood. Indeed, our initial intention was merely to show the utility of a new method of analysis with the inverstion doubling of ammonia as a standard for assay. The results of our analysis suggest that the inversion doubling is more complicated than an analysis which uses only one symmetry coordinate would encourage one to believe.

We report the results of an analysis of the inversion doubling which for the first time makes use of a symmetry-adaptable Taylor series expansion of the pair-wise intramolecular, interatomic interactions between the nitrogen atom and each atom of hydrogen. We show that a variational analysis, which is similar in part to that of Swalen and Ibers,[8] yields, by relatively easy computation, values for the splittings of the vibrational bands. We also find, interestingly enough, that through a selection of parameters for these pair-wise potentials we can bracket the experimental values for the splittings within a band or the separations between bands. However, it is apparently not possible with the analysis which we present to approach the experimental values of both the splittings and band separations simultaneously. This appears to be a manifestation of the contribution of other vibrational (or even perhaps, vibronic) degrees of freedom to the tunnelling.

In general, the method of analysis which we illustrate here finds use in the investigation of vibrational and rate processes, especially processes which

where $P_\ell(\mathbf{r}\cdot\mathbf{R})$ is the Legendre polynomial and $\mathbf{r}\cdot\mathbf{R} = \cos\theta$ with θ the angle between the vectors $\mathbf{r}$ and $\mathbf{R}$. The coefficient $A_{n\ell}$ is given in the previous paper, ref. (11). In eqn (3) $k_n(x)$ is the modified spherical Bessel function of the third kind.[11] It is clear that $r<R$.

If we restrict the motion of the nitrogen atom to be along the z-axis, then

$$V(z) = \sum_{n=0}^{\infty} C_n z^n \tag{4}$$

with

$$C_n = \frac{3Da^n}{n!} \sum_{\substack{\ell=0 \\ \text{even}}}^{n} A_{n\ell}(-1)^{\ell/2} \frac{(\ell-1)!!}{2^{\ell/2}(\ell/2)!} \Big\{ 2^n e^{2ar_0}\{2aR\, k_{\ell-1}(2aR) - (n-\ell)k_\ell(2aR)\}$$

$$- 2e^{ar_0}\{aRk_{\ell-1}(ar) - (n-\ell)k_\ell(aR)\}\Big\}. \tag{5}$$

It is necessary to consider the restriction $z<R$ in eqn (5) in the evaluation of matrix elements. Thus, for limits of integration which extend to infinity, one needs also to consider the quantity $\sum_{n=0}^{\infty} C_n(z)R^n$, when $z>R$. It is possible to show, however, that terms which involve this quantity contribute negligibly to the complete matrix element. Thus, eqn (4) can be used in the evaluation of matrix elements with the limits extended to infinity.

A variational calculation is considered in terms of a limited basis set of linear harmonic oscillator functions:

$$\phi_n(\alpha z) = \alpha\left(\frac{1}{2^n \pi^{\frac{1}{2}} n!}\right)^{\frac{1}{2}} \exp(-\tfrac{1}{2}\alpha^2 z^2) H_n(\alpha z) \tag{6}$$

where $H_n(x)$ is the Hermite polynomial and $\alpha = \sqrt{\mu\omega/\hbar}$ with μ the reduced mass. It is clear that ω (or α) can be regarded as a variational parameter in the calculation.

The matrix elements of z^n which arise from the use of eqn (4) are generated

take place in condensed phases.

Basic Analysis

In order to determine the splittings of the various vibrational states, we make use of a Morse potential to represent the interaction between an individual hydrogen atom and nitrogen. It is evident that there is no restriction to the Morse potential; any suitable function may be used.

The origin of coordinates is located at the centre of the equilaterial base triangle which is defined by the three hydrogen atoms of ammonia. The C_3 axis is defined to be the z-axis, and it is also simultaneously the transfer axis for nitrogen. The potential energy function is simply

$$V(z) = 3D \exp\{a(r_0-r(z))\}\Big(\exp\{a(r_0-r(z))\} - 2\Big) \tag{1}$$

where D is a dissociation energy and a is the usual parameter which is associated with this function. The distance r(z) is defined by

$$r(z) = (z^2 + R^2)^{\frac{1}{2}} \tag{2}$$

where R is the perpendicular distance from the origin on the C_3 axis to any of the three equivalent hydrogen atoms.

The expansion of the Morse potential in a Taylor series in spherical polar coordinates is[9,10]

$$V(r+R) = 3D \sum_{n,\ell} \frac{(ar)^n}{n!} A_{n\ell} P_\ell(\hat{r}\cdot\hat{R}) \Big\{ 2^n e^{2ar_0} (2aRk_{\ell-1}(2aR) - (n-\ell)k_\ell(2aR)\}$$

$$- 2e^{ar_0}\{aRk_{\ell-1}(aR) - (n-\ell)k_\ell(aR)\}\Big) \tag{3}$$

with the use of the recurrence relation for the Hermite polynomials:[11]

$$H_{m+1}(x) = 2xH_m(x) - 2mH_{m-1}(x). \tag{7}$$

Thus, (in dimensionless coordinates)

$$\langle k|q^n|\ell\rangle = 2^{-\frac{1}{2}}\Big\{(\ell+1)^{\frac{1}{2}}\langle k|q^{n-1}|\ell+1\rangle + \ell^{\frac{1}{2}}\langle k|q^{n-1}|\ell-1\rangle\Big\}. \tag{8}$$

One readily derives the matrix elements of order n from the elements of the lower order n-1.

The remaining matrix elements of p^2 are well-known[12] and need not be reproduced.

Results and Discussion

The results of four representative calculations (a distillate of many) to determine both the splittings and the separations between bands are collected in Table 1. Some interesting features are apparent upon the examination of these results.

To begin, we sought to attempt to relate the tunnelling to the vibrational frequencies for the symmetric stretching mode of the molecule in its ground state--the pyramidal structure. The pairwise N-H potential energy functions are related directly to this frequency. As the expansion, eqn (3), indicates, the potential energy functions which apply to the symmetric stretch also apply to the axial motion which is associated with the tunnelling. Thus, we believed, it ought to be relatively straightforward to assign the values of D and a in the Morse potential. Once assigned *via* the symmetric stretch, these quantities should apply to the tunnelling, as indicated. This proved not to be the case.

We found the following. First, the splitting can be adjusted by altering the bond lengths and the dihedral angle. Second, the spacings between the bands are related to the value which one assumes for the quantities D and a (these, as indicated, in turn can be related to the value of the frequency for the symmetric stretch). Finally, the variational quantity ω (or α) has little effect on either the splitting or the separation between bands for values of ω in the range $500cm^{-1} < \omega < 1{,}000cm^{-1}$.

We believe that the method of analysis which we set out to assay against the inversion of ammonia passes the test. It is clear from the results which are displayed in the table that a variational calculation, which is based upon the use of an expansion of the pairwise interactions in the evaluation of matrix elements, accounts for at least the greater part of the splittings. Moreover, in principle, it is an accurate form of analysis. If the inversion doubling involved only the ground vibronic state of the ammonia molecule, then the assignment of accurate values of the parameters for *any* parametric, pairwise potential energy function from the frequency of the symmetric stretch ought to apply with equal accuracy to the inversion doubling. It is clear that the Swalen-Ibers analysis[8] assigned values to parameters in a function which applies only to the tunnel transiton. Thus, it was possible for them to reproduce the splittings with high accuracy. Such a parametric representation can assimilate subtle vibronic interactions. Swalen and Ibers noted that a variation of the reduced mass as a function of angle improved the fit which they were able to obtain with the use of experimentsl data in a least squares analysis. They argued, as have others (see the discussion of this point in the Swalen-Ibers paper, ref. 8), that the tunnelling takes place with the N-H bond distance held at a constant value. Our results can be adjusted slightly by also varying the value of the reduced mass in accord with the suggestion of Swalen and Ibers. However, we find other sensitivities to bond angle and distance; thus, the adjustment

is not a simple one. We believe that there emerge, through the lack of easy agreement between our analysis and the experimental data, indications of the role played by other vibrational degrees of freedom and, perhaps, even other vibronic states.

The results of our investigation suggest that in the process of inversion, the hydrogen atoms in the base plane of ammonia shift slightly to occupy positions at the vertices of an expanded triangle. The tunnelling does not simply involve the migration of the nitrogen atom through the centre of the plane of rigidly held hydrogen atoms. This conclusion, of course, is in agreement with that reached by Swalen and Ibers[8] and others. The difference, however, between their treatment and ours is that by means of an adjustment of the reduced mass, Swalen and Ibers were able to obtain good agreement with experiment. In our treatment, it is apparent that a simultaneous optimization of the H-H distances together with the treatment of the tunnel transition shall have to be carried out in order to obtain agreement with experiment both for the splittings and the separations between bands. Moreover, such a calculation must take into consideration the inherent anharmonicity of the interactions.

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Table 1

State	Calc(1)	$\Delta^{\pm}$	Calc(2)	$\Delta^{\pm}$	Calc(3)	$\Delta^{\pm}$	obs*	$\Delta^{\pm}$
0^+	0.0		0.0		0.0		0.0	
		0.78		0.81		0.31		0.79
0^-	0.78		0.81		0.31		0.79	
1^+	1,006.64		1,223.40		1,219.00		932.51	
		34.02		35.00		15.00		35.81
1^-	1,040.06		1,258.40		1,234.00		968.32	
2^+	1,737.31		2,121.70		21.65.70		1,597.60	
		282.18		316.80		206.20		312.40
2^-	2,019.49		2,438.50		2,371.90		1,910.00	
3^+	2,556.32		3,085.50		3,005.6		2,383.46	
		532.68		528.90		547.20		512.02
3^-	3,089.00		3,614.40		3,552.80		2,895.48	

(* from ref. 2)

Parameters used in the calculations

	(1)	(2)	(3)
μ(reduced mass)	2.55	2.55	2.55
D(N-H dissociation energy)	27,992 cm^{-1}	27,992 cm^{-1}	27,992 cm^{-1}
r_e(N-H bond length)	1.0116 Å	1.0116 Å	1.0116 Å
θ (N-H bond angle)	22^o	22^o	22^o
a (Morse exponent)	2.0485 A^{-1}	2.4723 A^{-1}	2.4723 A^{-1}
γ (vatlational parameter/ω=850cm^{-1})	8.01	8.01	8.91
ω_{NH}(N-H stretch)	2,900 cm^{-1}	3,500 cm^{-1}	3,500 cm^{-1}
λH(barrier height)	1,988 cm^{-1}	2,985 cm^{-1}	2,985 cm^{-1}

Addendum to Table 1

a and α calculated according to the formulae

$$a = \omega_{NH}\sqrt{\mu/2D}$$

$$\alpha = \sqrt{\mu\omega/\hbar}$$

The height of the barrier to tunnelling is found from

$$\Delta H = 3D\left(e^{a(r_0-R)} - 1\right)^2$$

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